

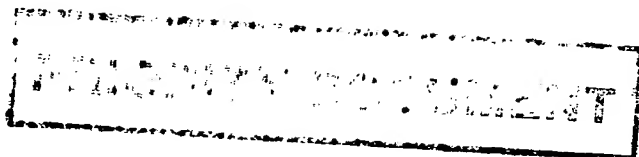


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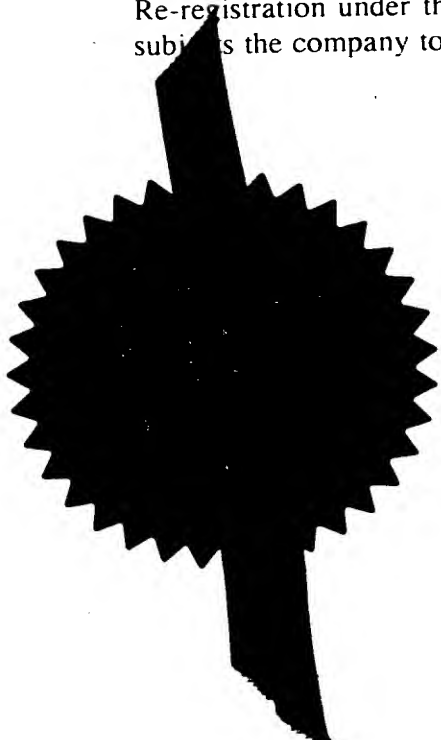
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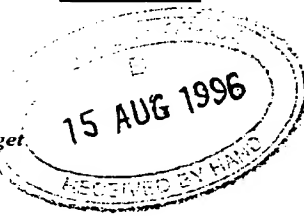
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Cardiff Road
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1. Your reference

MGH/MG/PO6346GB

2. Patent application number

(The Patent Office will)

9617181.4

15 AUG 1996

3. Full name, address and postcode of the or of each applicant (underline all surnames)

W.L. GORE & ASSOCIATES (UK) LTD.
1 Bell Yard
LONDON
WC2A 2JP

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

667679 6001

4. Title of the invention

WATER-VAPOUR-PERMEABLE LAYERED MATERIAL

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

CRUIKSHANK & FAIRWEATHER
19 Royal Exchange Square
GLASGOW G1 3AE

Patents ADP number (if you know it)

547002 ✓

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Country

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Claim(s)	4
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Any other documents (please specify)

11. I/We request the grant of a patent on the basis of this application.

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CRUIKSHANK & FAIRWEATHER 14/08/96

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WATER-VAPOUR-PERMEABLE LAYERED MATERIAL

The present invention relates to a flexible water-resistant water-vapour-permeable layered material, particularly for use in garments, which exhibits a combination of good breathability (i.e. water vapour transmission) and good durability.

Water-vapour-permeable laminate materials which are resistant to liquid water penetration are known from US patents 3,953,566 and 4,194,041. The former refers to the production of an expanded porous polytetrafluoroethylene (PTFE) membrane. Such membranes generally have intrinsically poor abrasion resistance (see Table 1 herein). The latter discloses a material which comprises a porous membrane (particularly expanded PTFE) provided on one surface thereof with a continuous layer of a hydrophilic material which is water-vapour-permeable, such as a polyurethane. Other water-resistant water-vapour-permeable materials are also commercially available and these include polyurethane coatings applied to a fabric, polyurethane membranes laminated to a fabric, and polyester membrane-fabric combinations.

Such materials often include an inner liner which protects the polyurethane-coated face of the material in use. The preformed liner is generally laminated to the polyurethane-coated face by means of a layer of adhesive.

However, the liner adds to the cost, weight and bulk of the material. In some applications, it may be desirable to eliminate the liner. However, this has the disadvantage of exposing the polyurethane directly to abrasive forces.

US patent 5,026,591 discloses coating a scaffold material (expanded PTFE or microporous polypropylene) with a continuous coating of a hydrophilic material (hot melt hydrophilic polyurethane or polyurethane acrylate) and pressing directly into the coating a substrate material (a polyamide non-woven, a polycotton woven blend etc.) and then allowing the coating to cure. The objective is to provide a continuous coating of hydrophilic material without any leaks therein, sandwiched between the scaffold material and the substrate.

US patent 4,925,732 discloses the production of a laminate for making shoes composed of a pair of moisture permeable materials (e.g. leather and fabric) adhered together by means of a moisture permeable adhesive (e.g. a polyurethane adhesive).

European patent EP 0465817 discloses a laminate for use in protective materials comprising an expanded PTFE liquid barrier layer, having a water-vapour permeable adhesive layer thereon, and active carbon beads and a net partially embedded in the adhesive layer. The net

however remains above the surface of the adhesive so as to protect the active carbon beads from being mechanically dislodged. The net thickness is typically about 0.5mm (500 microns).

It is an object of the present invention to provide good abrasion resistance in water-resistant water-vapour-permeable layered materials, without the need for a protective liner.

The present invention provides a flexible water-resistant water-vapour-permeable layered material, which comprises:

- a water-resistant water-vapour-permeable flexible substrate material; and
 - a discontinuous layer having been formed on said substrate material such as to be bonded thereto, and to constitute a protective surface layer of the layered material;
- the layer comprising a discontinuous pattern of material, the discontinuous pattern including open areas free of said material.

The invention also relates to a process of producing the layered material.

Water-resistant materials which resist liquid water penetration are well known to persons skilled in the art of making rainwear and the term is to be construed accordingly. Clearly, the degree of water-resistance

required in a so-called waterproof garment depends upon the severity of the climatic conditions to which it is subjected. A suitable test of water-resistance (Suter test) is described herein. A practical indication of water-resistance is that water is not forced through the sample by a pressure of 1.4 pounds per square inch (0.1kg/cm^2), or more typically 2.0 pounds per square inch (0.14kg/cm^2). This also gives a measure of hydrophobicity in respect of porous materials.

The benefit of a water-vapour-permeable material is that perspiration from the wearer's body is allowed to escape from within the garment by passage through the material, thus preventing build-up of liquid water within the garment and consequent clammy feeling. In order to be considered as water-vapour-permeable, the flexible substrate should generally have a water-vapour-permeability of at least 1,000, for example 1500 to 35,000 (preferably 3000 to 10,000) $\text{g/m}^2/\text{day}$. However, values in excess of 100,000 $\text{g/m}^2/\text{day}$ are possible with certain substrate materials. The overall water-vapour-permeability of the flexible layered material will usually be somewhat lower than this (e.g. 5000 to 12,000 $\text{g/m}^2/\text{day}$ or up to 30,000 g/m^2 for certain substrates) in view of the presence of the abrasion-resisting layer, but generally speaking its water-vapour-permeability may also be within the ranges outlined above.

A suitable water-resistant water-vapour-permeable flexible substrate material is disclosed in US patent 3,953,566 which discloses a porous expanded polytetrafluoroethylene (PTFE) material. The expanded porous PTFE has a micro-structure characterised by nodes interconnected by fibrils. If necessary, the water-resistance may be enhanced by impregnating the expanded PTFE with an hydrophobic impregnant (such as a low molecular weight perfluoro compound, for example a perfluoroalkyl acrylate or methacrylate). Such impregnants are also oleophobic and inhibit contamination of the porous PTFE by oils from the body of the wearer. This has the effect of coating the nodes and fibrils of the porous PTFE.

The water-resistant water-vapour-permeable substrate material might be a microporous material such as a high molecular weight microporous polyethylene or polypropylene.

Alternatively, the water-resistant water-vapour-permeable flexible substrate material may comprise a water-resistant water-vapour-permeable hydrophilic film of the type disclosed in US patent 4,194,041. Such films are generally also oleophobic. Certain hydrophilic polyurethane films have sufficient mechanical strength to be used unsupported. However, such hydrophilic layer may also be applied (e.g. as a coating) to an underlying

flexible membrane to form a composite substrate material. The flexible membrane may be formed of porous expanded PTFE as described in US Patent 3,953,566 and available under the GORE-TEX trademark. In this case, the hydrophilic material may also partially or completely fill the voids in the expanded PTFE structure. However, the hydrophilic layer may be supported on membranes of other woven or non-woven materials and a wide variety of such materials are known in the art.

Finally, the water-resistant water-vapour-permeable flexible substrate material may itself be laminated by known techniques to a woven or non-woven or knitted face fabric, such as a nylon or polyester fabric which in use constitutes the outer surface of the garment, and provides the required visual appearance and necessary mechanical properties.

Such materials as described above are essentially conventional. The contribution made by the present invention is to provide a discontinuous abrasion-resisting layer over the flexible substrate material so as to provide a protective surface layer which protects the water-vapour-permeable flexible substrate material from abrasion forces in a particularly lightweight, convenient and economical manner. Thus, it is surprisingly found that the application of an abrasion resisting layer, comprising a discontinuous pattern of

abrasion-resisting material (usually a polymeric material) is in itself sufficient to provide abrasion resistance and durability, without the need to apply the conventional inner liner. The abrasion-resisting polymeric material constitutes the surface layer of the layered material and is generally the layer which is innermost when the material is used to form a garment, that is to say it is the surface layer which is closest to the skin of the wearer. It has been surprisingly found that the discontinuous pattern of abrasion-resisting material, whilst providing the necessary moisture vapour permeability, is sufficient to resist abrading of the material during flexing thereof, both against itself and against any other materials which may be present (for example other garments worn by the wearer).

It has been found essential to lay down the abrasion-resisting polymeric material directly onto the flexible substrate material such as to form the abrasion-resisting layer in situ. The use of preformed materials as the abrasion-resisting layer has been found to be unsatisfactory. Convenient application methods include screen printing, gravure printing and spraying. This results in an intimate bond being formed between the abrasion-resisting layer and the flexible substrate material, whilst at the same time allowing a suitably

thin layer of abrasion-resisting material to be applied. The polymeric material may be applied to selected areas of the substrate material in liquid form from a hot melt, by solution coating or emulsion coating. The liquid polymeric material may include a prepolymer which cures in situ, a UV light curable polymer, a room temperature vulcanising polymer, or a thermoplastic polymer. Suitable elastomeric polymers include polyesters, polyvinylchloride, polyamides, silicones, polyurethanes, or polyurethane-polyester composites. Reactive polyurethanes, such as blocked polymers, whose reactive groups unblock above a certain temperature are especially useful. Fillers may be included provided their particle size is less than the smallest dimension of the discontinuous layer. The cured polymer will generally be resistant to conventional dry-cleaning solvents. Where the substrate material includes a hydrophilic coating layer, the abrasion resisting polymer when cured will be chemically compatible therewith.

The abrasion resisting polymer may itself be water-vapour-permeable; though this is generally not necessary provided that the percentage coverage of the substrate material is not too great to substantially affect the water-vapour-permeability thereof.

The discontinuous pattern of abrasion-resisting material is discontinuous in the sense that it includes

open areas free of polymeric material and does not form a continuous layer. Generally, the percentage coverage of the flexible substrate material by polymer is in the region 20-80%, particularly 30-70%, more especially 40-60% by area.

The discontinuous pattern may be any suitable pattern (preferably a regular pattern), such as a pattern of dots, lines or meshes. The pattern needs to be chosen so as to exhibit good handleability and to prevent the overall layered material becoming unduly stiff, and for this reason patterns of dots are preferred. The dots may in principal be of any cross-section, such as squares, rectangles, polygons etc. However, in order to minimise abrasion-resistance, squares, diamonds or other shapes having sharp corners are not preferred. Preferably, the dots are roughly hemispherical, part-spherical or truncated hemispherical in shape. Another useful abrasion-resisting pattern is formed from a line of interconnected dots, referred to as a helioklisiograph pattern (e.g. see Figure 6 herein).

The pattern of dots may be a random pattern or an orderly pattern according to some predetermined spatial geometry. Each dot is preferably of a maximum cross-sectional diameter which is less than 5000 microns, for example is in the range 100 to 1000 microns, preferably 200-800, particularly 400-600 microns. The dots may be

spaced apart centre-to-centre by 200-2000 microns, particularly 300-1500, especially 400-900 microns. Each dot generally has a height in the range 10-100 microns, preferably 20-80, particularly 35-70 microns.

In the first instance, abrasion forces lead to the creation of leaks in the water-resistant layered material. This destroys the water-resistance of a garment constructed from the layered material. An appropriate test methodology for determining abrasion-resistance for present purposes is to measure the degree of abrasion until one or more leaks is formed in the material. Abrasion testing and water-resistance may be determined using methodologies as set out herein. The abrasion-resistance of the material according to the present invention (including the abrasion-resisting layer) has an abrasion-resistance which is greater (within experimental limits) than the flexible substrate material without the abrasion-resisting layer. Depending on the nature of the abrasion-resisting layer, the abrasion resistance of the material according to the present invention may be at least 1.5 times, advantageously at least 4.0 times, the abrasion-resistance of the flexible substrate material alone. In particular circumstances, the abrasion-resistance may be increased by up to 10 times or more. On the other hand, whilst the moisture vapour permeability of the substrate

material is decreased somewhat by the application of the abrasion-resisting layer (which could itself have a degree of water vapour permeability), such decrease would be also expected from the lamination of an inner lining to the substrate material as in conventional technology. Thus, the use of an abrasion-resisting layer according to the present invention has the capacity to markedly increase the abrasion resistance of the material whilst at the same time not unduly decreasing the water-vapour-permeability.

It is surprisingly found that the decrease in water vapour permeability is less than the decrease in free surface area of the substrate material due to application of the abrasion resisting layer.

The material of the present invention may be used to produce garments, hats, gloves, shoes etc.

An important feature of the water-vapour-permeable water-resistant layered materials of the present invention is their ability to be seam sealed. This is carried out in order to seal the stitched seams of a water-resistant garment to prevent liquid water entering through the stitching holes. It is accomplished by applying a tape coated with a heated hot melt adhesive under pressure over the inside of the seam and bonding thereto. However, the seam-sealing of conventional 3-layer materials is impeded by the presence of the inner

liner which lies between the water-resistant membrane and the sealing tape, and which hinders the formation of a seal between the membrane and the tape.

It is found that the materials of the present invention have good seam sealing properties and adhesion of the seam sealing tape to the abrasion-resisting layer is good.

Embodiments of the present invention will now be described by way of example only.

Figures 1a and 1b are cross-sectional views to an enlarged scale of embodiments of the invention without a face fabric;

Figure 2 is a cross-sectional view to an enlarged scale of a further embodiment of the invention including a face fabric (so-called $2\frac{1}{2}$ layer material);

Figure 3 is a schematic diagram of a coating apparatus for applying the abrasion-resisting polymer layer onto the substrate material;

Figure 4 shows to an enlarged scale (50:1 magnification) the repeat pattern of recesses on the gravure roller of Figure 3 used to apply the polymer dot pattern onto the substrate material;

Figure 5 is a cross-section to an enlarged scale (magnification 100:1) of a single recess showing dimensions in microns; and

Figure 6 is a detail to an enlarged scale of the

pattern on a helioklisiograph roller for applying the abrasion-resisting polymeric material.

Figure 1a shows a waterproof water-vapour-permeable flexible substrate material 2 having applied thereto an abrasion-resisting layer 4 composed of individual dots 6 of polymeric material firmly adhered thereto. The flexible substrate material is composed of an expanded PTFE membrane produced as described in US 3,953,566. The membrane has a maximum pore size of 0.2 microns as determined by bubble point measurements (see US 5,026,591 Henn) and a weight of 15g/m². The abrasion-resisting layer is applied by gravure printing the pattern of dots using a hot melt polymeric material onto the substrate material. A face fabric (not shown) may have been laminated to the other face of the expanded PTFE membrane in conventional manner.

Figure 1b shows a cross-section through a further embodiment of the invention wherein the flexible substrate material 2 is a composite formed of a first layer 8 of an expanded PTFE membrane of the type discussed in relation to Figure 1, having thereon a hydrophilic coating 10 of a water-resistant water-vapour-permeable material (for example a water-vapour-permeable polyurethane of the type disclosed in US 4,194,041 Gore). Such material is available under the trade mark GORE-TEX from W.L. Gore & Associates. The abrasion-resisting

layer 4 in this case is applied by gravure printing onto the hydrophilic layer 10 so as to be firmly adhered thereto. As shown in Figure 2 a face fabric 12 may have been applied onto the other face of the PTFE membrane to form a $2\frac{1}{2}$ layer material.

Figure 3 shows a coating apparatus for gravure printing the abrasion-resisting layer of polymeric material onto the flexible substrate material. The construction of the apparatus and its mode of operation follow the general disclosure of US5,026,591. A roll of expanded PTFE membrane is unwound and fed over a brake roller B which serves to apply a constant tension thereto, and over an idler roller I into the nip between a pressure roller P and a gravure roller G. The gravure roller has a pattern of recesses thereon for receiving liquid polymeric material and applying this to the substrate material membrane. The liquid polymeric material is applied onto the gravure roller by means of a doctor blade assembly D which applies the liquid polymeric material to the surface of the gravure roller and wipes excess material therefrom, such that the recesses in the surface of the gravure roller are filled with liquid polymeric material. Further rotation of the roller enables the polymeric material to be gravure printed onto one side of the substrate material membrane. The membrane with the applied polymeric layer is then

passed over a bowed roller BR and thence around an oil-filled hot roller H which effects curing of the polymeric material at elevated temperature. The layered material so formed is then fed off over a series of idler rolls I and a load cell roller L which monitors tension in the continuous web of layered material. Cooling occurs as the layered material passes over cooling can C, which is typically filled with cold water. The layered material is hauled off over a further idler roller I by which time the abrasion-resisting polymeric material has at least partially cured to a solid mass, thereby allowing the layered material to be rolled up.

As mentioned, the flexible substrate material may be in the form of an expanded PTFE membrane, optionally carrying a hydrophilic water-vapour-permeable coating, (e.g. a hydrophilic polyurethane) or one of the other materials described above. More usually, this membrane is itself pre-laminated to a face fabric prior to application of the abrasion-resisting layer.

Figure 4 shows a repeat pattern of recesses in the gravure roller G including dimensions in microns. The pattern comprises spherical segments arranged in a seven cell rosette. Details of the depression geometry (referred to as "cells") have the following nominal values:

material at elevated temperature. The layered material so formed is then fed off over a series of idler rolls I and a load cell roller L which monitors tension in the continuous web of layered material. Cooling occurs as the layered material passes over cooling can C, which is typically filled with cold water. The layered material is hauled off over a further idler roller I by which time the abrasion-resisting polymeric material has at least partially cured to a solid mass, thereby allowing the layered material to be rolled up.

As mentioned, the flexible substrate material may be in the form of an expanded PTFE membrane, optionally carrying a hydrophilic water-vapour-permeable coating, (e.g. a hydrophilic polyurethane) or one of the other materials described above. More usually, this membrane is itself pre-laminated to a face fabric prior to application of the abrasion-resisting layer.

Figure 4 shows a repeat pattern of recesses in the gravure roller G including dimensions in microns. The pattern comprises spherical segments arranged in a seven cell rosette. Details of the depression geometry (referred to as "cells") have the following nominal values:

	<u>Seven cell rosette</u>	<u>helioklisiograph</u>
Cell depth	- 100 microns	ca 65 microns
Cell diameter	- 500 microns	ca 290 "
Rosette diameter	- 1460 microns	-
Cell pitch in rosette	- 730 microns	ca 307
Cell coverage	- 41% by area	-

Figure 5 shows a cross-section of a single cell. The depression has part spherical geometry of a radius 369 microns.

Figure 6 shows a segment of helioklisiograph gravure roller pattern. The pattern is formed by spark erosion techniques onto the surface of the gravure roller such as to comprise a series of circular depressions 20 of dimensions given above interlinked by channels 22 (50 microns wide and 3 microns deep). The pattern extends spirally around the gravure roller.

TEST METHODSMOISTURE VAPOUR TRANSMISSION RATE (MVTR)(Potassium Acetate Method)

A description of the test employed to measure moisture vapour transmission rate (MVTR) i.e. water-vapour-permeability, is given below.

In the procedure, approximately 70ml of a solution consisting of 35 parts by weight of potassium acetate and 15 parts by weight of distilled water was placed into a 133ml. polypropylene cup, having an inside diameter of 6.5cm at its mouth. An expanded polytetrafluoroethylene (PTFE) membrane having a minimum MVTR of approximately $85,000\text{g/m}^2/24\text{hrs.}$ as tested by the method described in US Patent 4,862,730 to Crosby and available from W.L. Gore & Associates, Inc. of Newark, Delaware, was heat sealed to the lip of the cup to create a taut, leakproof, microporous barrier containing the solution.

A similar expanded PTFE membrane was mounted to the surface of a water bath. The water bath assembly was controlled at 23°C plus or minus 0.2°C , utilising a temperature controlled room and a water circulating bath. The sample to be tested was allowed to condition at a temperature of 23°C and a relative humidity of 50% prior to performing the test procedure. Three samples were placed so each sample to be tested was in contact with

the expanded polytetrafluoroethylene membrane mounted over the surface of the water bath, and was allowed to equilibrate for at least 15 minutes prior to the introduction of the cup assembly.

The cup assembly was weighed to the nearest 1/1000g and was placed in an inverted manner onto the centre of the test sample.

Water transport was provided by the driving force between the water in the water bath and the saturated salt solution providing water flux by diffusion in that direction. The sample was tested for 20 minutes and the cup assembly was then removed, and weighed again to within 1/1000g.

The MVTR of the sample was calculated from the weight gain of the cup assembly and was expressed in grams of water per square meter of sample surface area per 24 hours.

The above procedure was used for Example 2. For Example 4 the test was carried out using a ratio of potassium acetate to water of 600:185.

ABRASION TESTING

Abrasion testing was carried out using a Martindale Abrasion machine and rubbing samples with standard wool toll SM25 which complied with draft ISO ST CD 12974-1

Table 1, clause 5.6.2 which is based on British Standard BS 5690, 1991.

Briefly, the test procedure was as follows. Circular specimens of sample material were abraded on a reference abradant of a cross-breed worsted spun plain-woven wool fabric under pressure of 12kPa with a cyclic planar motion in the form of a Lissajous figure, which is the resultant of two simple harmonic motions at right angles to each other. The resistance to abrasion corresponds to the number of cycles to the defined end point. The abrasion machine was of the type described by Martindale (J.Text. Inst. 1942:33, T151).

Each sample was then removed from the machine after a predetermined number of rubs and tested for liquid water-resistance as described herein (under a hydrostatic pressure of 2 psi (0.14 kg/cm²) for 3 minutes) until a leak was detected which indicated breakdown of water-resistance. Samples were tested every 100 rubs up to a 1000 rubs. They were then tested as follows:

every	2000 rubs	up to	20,000 rubs
then every	5000 "	"	50,000 "
then	" 10,000 "	"	100,000 "
and then	" 20,000 "		.

WATER-RESISTANCE (SUTER TEST)

Samples of the present invention were tested for water-resistance using a modified Suter test apparatus, which is a low water entry pressure challenge. The test procedure is set out in BS3424, method 29C. Water was forced against the underside of a sample of 11.25cm diameter sealed by two circular rubber gaskets in a clamped arrangement. As appropriate, the sample was mounted with the hydrophilic coating downwards against the water, the expanded porous polytetrafluoroethylene membrane being uppermost. It is important that a leakproof seal is formed by the clamp mechanism, gaskets and sample. In deformable samples, the sample was overlaid by a reinforcing scrim (e.g. an open non-woven fabric) clamped over the sample. The upper side of the sample was open to the atmosphere and visible to the operator. The water pressure on the underside of the sample was increased to 2 pounds per square inch (0.14 kg/cm²) by a pump connected to a water reservoir, as indicated by a pressure gauge and regulated by an in-line valve. The upper side of the sample was visually observed for a period of three minutes for the appearance of any water which might be forced through the sample in the event of lack of water-resistance. Liquid water seen on the surface was interpreted as a deficiency in the water-resistance of the sample (i.e. a leak). The sample

passed the test if no liquid water was visible on the upper side of the sample within the three minute test period.

WASH TO LEAKAGE

The purpose of this test is to determine the time at which leakage occurs in laminated samples by continuous wet flex and abrasion over an extended period of time.

Full width samples of approx. 36cms in length are cut and the samples are trimmed on all 4 sides using pinking scissors. Where samples are likely to fray and cause tangling, all edges are sewn. Enough samples are cut to give a total wash load of 900 ± 90 gms. Make weight fabric samples can be added to make the total weight if not enough samples are available. Samples are then conditioned at $20 \pm 2^\circ\text{C}$ and $65 \pm 5\%$ relative humidity for 4 hours.

The conditioned samples are tested on a Calibrated Hydrostatic Head Tester at 5 positions across the width of the fabric to 1p.s.i. for 3 mins. to check for any leakage before washing. The positions are marked with an ink marker, so that the same positions can be tested every time. The machine will have a ramp rate of 60cms water pressure min. and samples will be tested at the 5 positions at 1p.s.i. for 3 mins.

Enough samples or samples plus make-weights are

prepared to make a total load of 900±90gms. for each machine. Samples are then washed according to the Kenmore wash method (QL 062). After approx. 72 hrs. wash the samples are hung to dry, conditioned, then Hydrostat~~position~~ tested at the same 5 to 1p.s.i. for 3 mins. The test site is deemed to have failed when the first small growing leak is observed. The wash/dry/test cycle is repeated until all 5 positions show signs of leaking.

KENMORE WASH METHOD (QL062)

This describes how the Kenmore wash machine Heavy duty 70 series was used to do continuous wet flex and abrasion testing.

The machine has a clear vented perspex cover to prevent the water temperature from exceeding 45°C with continuous washing. The temperature can be checked using a thermometer.

The machine had the water level control set at medium. The water temperature control was set to cold, and the machine cycle selector set at 14 which will give an agitation speed of 150-180 r.p.m. The auto/hand switch should be left on auto. The lid was closed with the isolator screwed fully in. The machine cycle selector knob was pulled out to make the machine fill with water until it reached a level at which the cut-off

switch engages. The isolator was unscrewed and 60±4 litres of water poured into the machine and the depth of water measured. After adding the required samples to a total wash load of 900±90g the lid was closed and the isolator screwed in. The wash cycle selector knob was operated to set the machine to wash mode. When ready to spin out the water, the control knob was operated and turned to spin. The water was drained from the machine. The isolator switch was unscrewed and the lid opened to inspect the samples.

The samples were checked approx. every 10 hours for tangling and untangled if required. Cold water added to keep the volume correct every 24 hrs. approx. and the load of fabrics should be a constant weight. The water temperature was not allowed to exceed 45°C.

EXAMPLE 1 (Production)

Employing the coating assembly described in relation to Figure 3 above, various flexible substrate materials were coated with abrasion-resisting polymeric material. Generally speaking, the flexible substrate materials comprising expanded PTFE had previously been laminated to a face fabric formed of woven texturised nylon or woven polyester. However, in an alternative method the face fabric can be laminated to the substrate after application of the abrasion resisting layer. The

abrasion resisting layer was a reactive hot melt, hydrophilic polyurethane (designated OLC-5T) prepared according to Example 1 of US patent 5,209,969. Polymer in liquid form at 60°C was applied by means of a doctor blade held at a temperature of 62°C onto the gravure roller whose temperature was 60°C. The hot melt adhesive applied by gravure printing was cured by passage around a hot roller of temperature 182°C heated by oil at a nominal temperature of 200°C. The continuous web of substrate material was passed through the coating apparatus at a speed of 15m/min and the web had a width of 140cm. The tension at the cooling can as measured by the load cell was 250 to 400N.

The gravure roller was patterned either with a 7-cell rosette pattern according to Figure 4 and 5 or with a helioklisiograph pattern according to Figure 6.

The cooled material was respooled onto a core.

EXAMPLE 2 (Testing)

Samples were produced according to the methodology described in Example 1 for materials as set out in the Table 1 employing expanded PTFE substrate materials which had been previously laminated to a face fabric, and identified as follows:

G100 - TAS2 TK-100 1A
G101 - TAS2 TP-100 1A
G102 - ISL 2TK-100 1A
G103 - ISL 2TP-100 1A

These materials are available from W.L. Gore & Associates (UK) Ltd. under the identification numbers set out above. The abbreviation TAS indicates that the face fabric is a woven texturised nylon fabric referred to as Taslan. The abbreviation ISL indicates that the face fabric is a woven polyester fabric (72 dTex and 75 filament yarn) referred to as Islay.

The material referred to as BTAS is equivalent to G101 but wherein the face fabric and the expanded porous PTFE substrate material are laminated according to a different methodology and referred to as Blue Taslight. The above materials G100 to G103 and BTAS comprise a face fabric laminated to an expanded PTFE membrane coated on its other surface with a continuous hydrophilic layer of a water-vapour-permeable polyurethane.

The material referred to in the table as PTAS comprises a Taslight face fabric laminated to a uncoated porous expanded PTFE membrane of 0.2 micron maximum pore size by bubble point determination and a weight of 15g/m².

In each case, three samples were tested (each in

triplicate). For comparison purposes, the plain 2-layer material (without abrasion-resisting layer) was tested according to the abrasion testing methodology as set out herein. Also tested were so-called $2\frac{1}{2}$ layer materials according to the present invention, comprising the comparison sample having applied thereon an abrasion-resisting layer of gravure-printed polymeric material according to either a helioklisiograph pattern ("helio") as in Figure 6; or a rosette pattern of dots ("dots") according to Figures 4 and 5.

Samples of the six materials were tested according to the Martindale abrasion testing technology set out herein. Failure of the material was determined as the point at which leaks were detected using the water-resistance test set out herein. The moisture vapour transmission rate was also determined as described herein. The results are set out in Table 1. It is clear from the table that substantial increases in abrasion resistance to leakage are obtained in the samples having the abrasion-resisting polymer layer according to either the helioklisiograph pattern or the dots pattern.

EXAMPLE 3 (Various Polymers)

Using the general production method of Example 1 various layered materials according to the invention were produced, which employed a number of different polymer

compositions as the discontinuous abrasion-resisting layer as follows.

The polymers were polyurethanes. OLC-5T was prepared according to the teachings of US patent 5,209,969. TB016 was prepared according to US patent 4,532,316. LB25 and LB31 are employed by W.L. Gore & Associates and have the following characteristics:

	Tensile at break (psi)	Elongation at break (%)	Modulus of elasticity (psi)	Viscosity (poise)
LB25	2130	1300	1000	5130
LB31	1290	1760	805	3890

(Tensile test is carried out according to ASTM method D638, specimen die IV and 2 inch/min crosshead speed. Viscosity test is carried out using a Tinius Olsen extrusion plastometer at 155°C, 5kg weight, 0.0825 inch diameter orifice and 0.315 inch length orifice.)

As described in Example 1, the polymer OLC-5T requires curing at elevated temperature (hot roller temperature 200-220°C and coating speed (10m/min). However, this is not required for the remaining three polymers, in which case the hot roller H was omitted. These three polymers are thermoplastic and were melted by heating to 160-180°C prior to application onto the gravure roller at substantially the same temperature, and then printed onto the expanded PTFE substrate (previously

laminated to a face fabric) and cooled. The speed of substrate material through the coating apparatus was 10m/min. The face fabric was either Islay, Taslan or Taslite (see Example 2). The so-called 2½ layer materials according to the present invention thus comprised the following layers:

a face fabric 12, a water-resistant water-vapour permeable flexible substrate 2 (expanded PTFE membrane coated with a water-vapour permeable polyurethane), and a discontinuous layer 4 of polymeric material; as shown schematically in Figure 2.

The polymer was printed according to a 7-cell rosette pattern of the type shown in Figure 4.

EXAMPLE 4 (Properties)

The properties of the various layered materials according to the invention as described in Example 3 were determined as described herein. These were compared to conventional 2-layer (face fabric and flexible substrate) and 3-layer (face fabric, flexible substrate and inner liner knit) constructions. The various constructions are summarised in Table 2 together with water-vapour-permeability results (MVTR) and durability results (Martindale abrasion tests and Wash to leaks tests).

As would be expected, the water-vapour-permeability (MVTR) of the 2½ layer material of the present invention

is intermediate that of conventional 2-layer and 3-layer constructions. As regards durability, the Martindale abrasion test results are to some extent dependent on face fabric and the technique used to laminate the face fabric to the water-vapour permeable substrate material, but generally speaking the abrasion resistance is improved in the $2\frac{1}{2}$ layer materials of the present invention over conventional 2-layer materials. Wash to leaks is another durability test which measures the time to leakage in a sample subjected to a continuous flex and abrasion under wet washing conditions. The wash durability of the materials of the present invention is at least as good as that of the conventional material.

Variation of the polymer print pattern (using OLC-5T adhesive) resulted in minor variations in water-vapour-permeability of the inventive materials.

The $2\frac{1}{2}$ layer material of the present invention has generally been found to possess the durability normally associated with conventional 3-layer materials but with the comfort, handle and production costs of a conventional 2-layer material. Water-resistant garments require to have their stitched seams sealed with tape to prevent water ingress. The seam sealing properties of the present materials are good and comparable to conventional 2-layer materials.

TABLE 1

MARTINDALE ABRASION RESULTS
HYDROSTATIC HEAD TEST TO 2 P.S.I.

SAMPLE		RUBS	LEAKS	M.V.T.R. g/m ² /24hr
100	- plain	2000	3 leaks	12,110
	- helio	8000	1 leak	7,580
	- dots	9000	leak	8,620
101	- plain	2000	multiple leaks	15,050
	- helio	14000	multiple leaks	8,380
	- dots	12000	multiple leaks	11,170
102	- plain	200,000	1 leak	14,300
	- helio	180,000	1 leak	7,220
	- dots	282,000	1 leak	8,400
103	- plain	7000	1 leak	14,230
	- helio	58000	1 leak	7,120
	- dots	62000	1 leak	11,070
BTAS	- plain	10000	3 leaks	12,520
	- helio	25000	2 leaks	5,200
	- dots	67000	1 leak	8,340
PTAS	- plain	300	7 leaks	24,850
	- helio	400	1 leak	20,840
	- dots	500	4 leaks	20,160

TABLE 2

<u>Construction</u> <u>/face fabric</u>	<u>Polymer</u>	<u>MVTR</u> <u>(s.d.)</u>	<u>Martindale</u> <u>abrasion</u>	<u>Wash to</u> <u>leaks</u>
<u>Compression</u>				
2 layer Taslan	-	11817 (2219)	3000	557
2 layer Islay	-	-	6000	-
3 layer Taslan	-	6186 (821)	-	-
<u>Invention</u>				
2½ layer Taslan	OLC-5T	7889 (894)	30,000	657
2½ layer Islay	OLC-5T	7810 (630)	>80,000	747
2½ layer Taslite	LB25	9848 (109)	45,000	761
" " "	LB31	10,051 (464)	3,000	629
" " "	TB016	8714 (519)	3,000	802

MVTR (moisture vapour transmission rate) is g/m²/24hr
 Martindale abrasion is number of cycles (rubs) to
 occurrence of a first leak.

Wash to leaks is hours of washing up to the occurrence of
 a leak according to wash to leakage test method described
 herein.

The results are generally the mean of five samples.

CLAIMS

1. A flexible water-resistant water-vapour-permeable layered material, which comprises

- a water-resistant water-vapour-permeable flexible substrate material; and
- a discontinuous layer having been formed on said substrate material such as to be bonded thereto, and to constitute a protective surface layer of the layered material; the layer comprising a discontinuous pattern of material, the discontinuous pattern including open areas free of said material.

2. A layered material according to claim 1 wherein the water-resistant water-vapour-permeable flexible substrate material has a water-resistance in excess of 0.1 kg/cm^2 .

3. A layered material according to claim 1 or 2 wherein the water-resistant water-vapour-permeable flexible substrate material has a water-vapour-permeability in excess of $1500 \text{ g.m}^2/\text{day}$.

4. A layered material according to any preceding claim wherein the substrate material is an expanded polytetrafluoroethylene (PTFE) membrane.

5. A layered material according to any of claims 1 to 3 wherein the substrate material is an expanded PTFE membrane impregnated with a polymeric hydrophobic and oleophobic material.
6. A layered material according to any of claims 1 to 3 wherein the substrate material is an expanded PTFE membrane having a hydrophilic layer coated thereon.
7. A layered material according to any of claims 1 to 3 wherein the substrate material is an unsupported water-vapour-permeable hydrophilic film.
8. A layered material according to any of claims 1 to 3 wherein the substrate material comprises a woven or non-woven or knitted material coated with a water-vapour permeable hydrophilic layer.
9. A layered material according to claim 6, 7 or 8 wherein the hydrophilic layer or film is formed of a polyurethane.
10. A layered material according to any preceding claim which further comprises a face fabric laminated to the substrate material such that the discontinuous layer

forms one surface of the layered material and the face fabric forms the other surface of the layered material.

11. A layered material according to any preceding claim wherein the discontinuous layer is formed of a polymeric material.

12. A layered material according to claim 11 wherein the polymeric material is a thermoplastic or a curable polyurethane.

13. A layered material according to claim 11 or 12 wherein the polymeric material is water-vapour-permeable.

14. A layered material according to claim 11, 12 or 13 wherein the discontinuous layer has a coverage of 30 to 70% by area of the substrate material, the balance being said open areas.

15. A layered material according to any preceding claim wherein the discontinuous layer is in the form of a pattern of dots.

16. A layered material according to claim 15 wherein each dot is roughly hemispherical in shape.

17. A layered material according to claim 15 or 16 wherein each dot has a maximum diameter in the range 200 to 800 microns.
18. A layered material according to any preceding claim having a water-vapour permeability of 5000 to 30,000 g/m²/day.
19. A garment, glove, hat or shoe which comprises the layered material of any preceding claim.
20. A process of producing a flexible water-resistant water-vapour permeable layered material which comprises coating a water-resistant water-vapour-permeable flexible substrate material with a discontinuous layer of protective material such that the protective material is bonded to the substrate material and constitutes a protective surface of the layered material; the layer comprising a discontinuous pattern of material including open areas free of material.

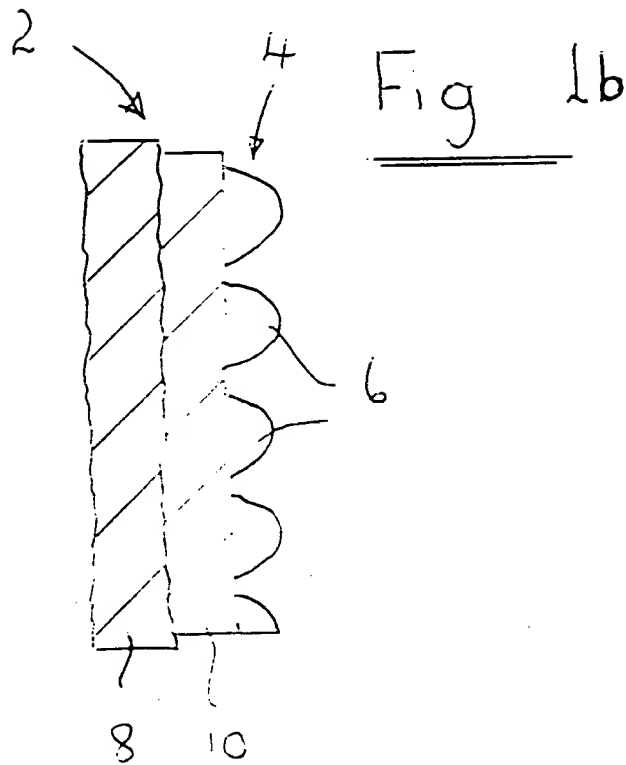
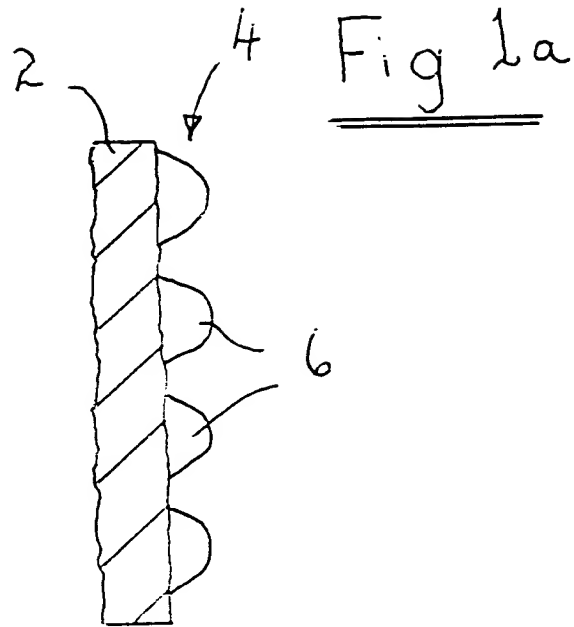


Fig 2

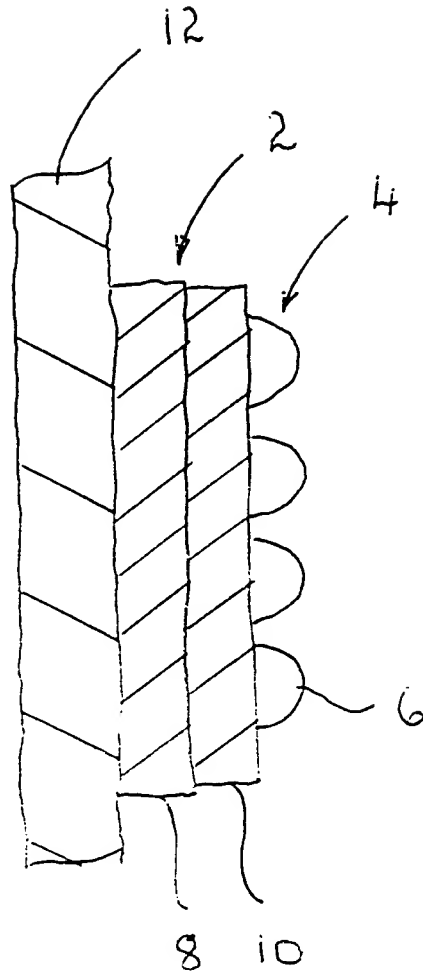


Fig 3

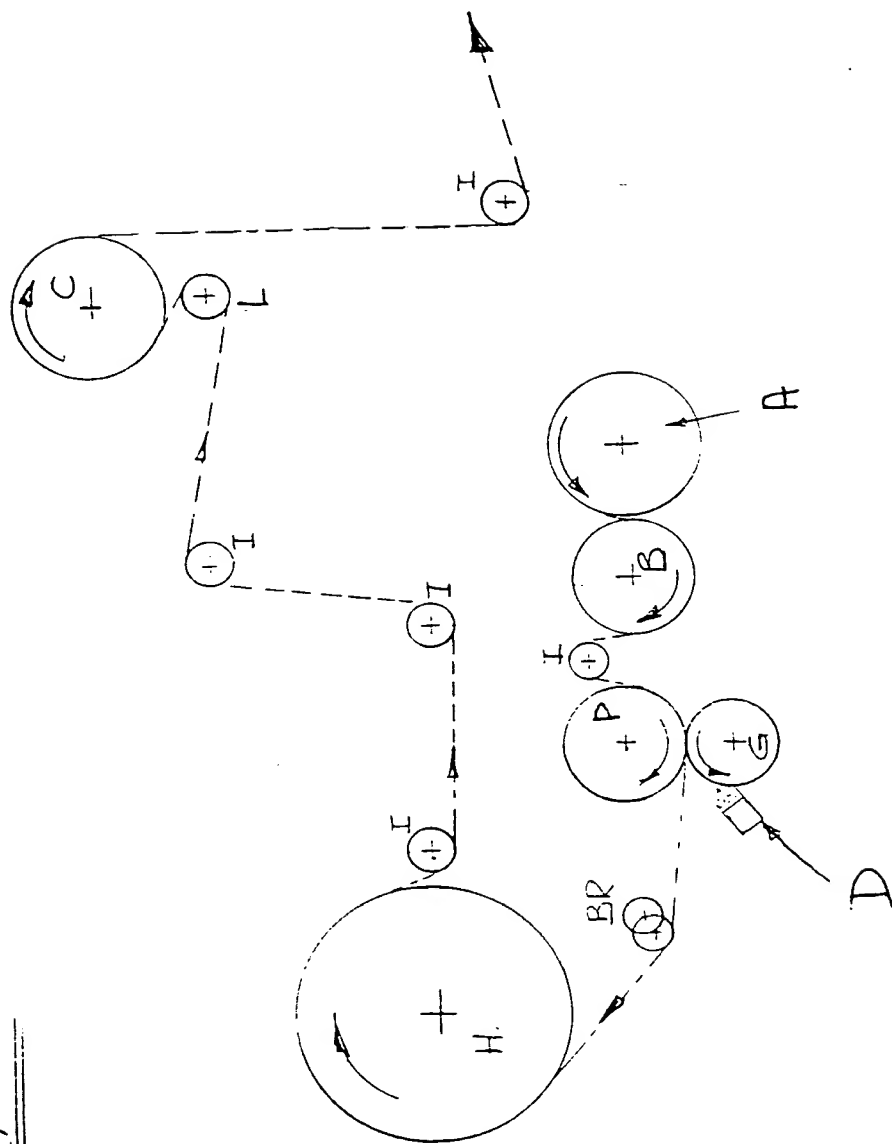


Fig 4

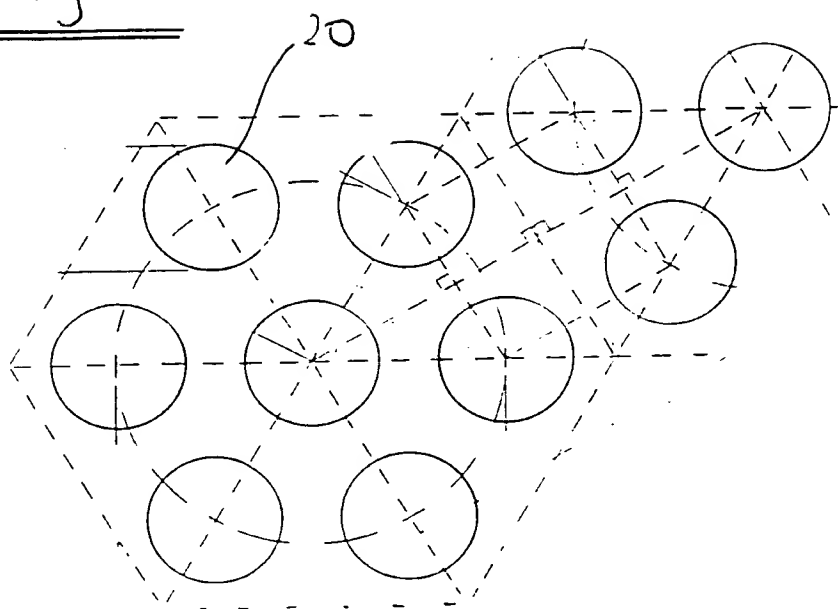


Fig 5

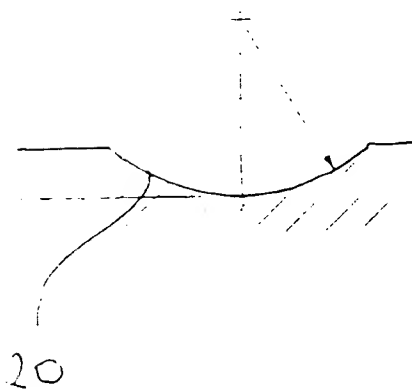
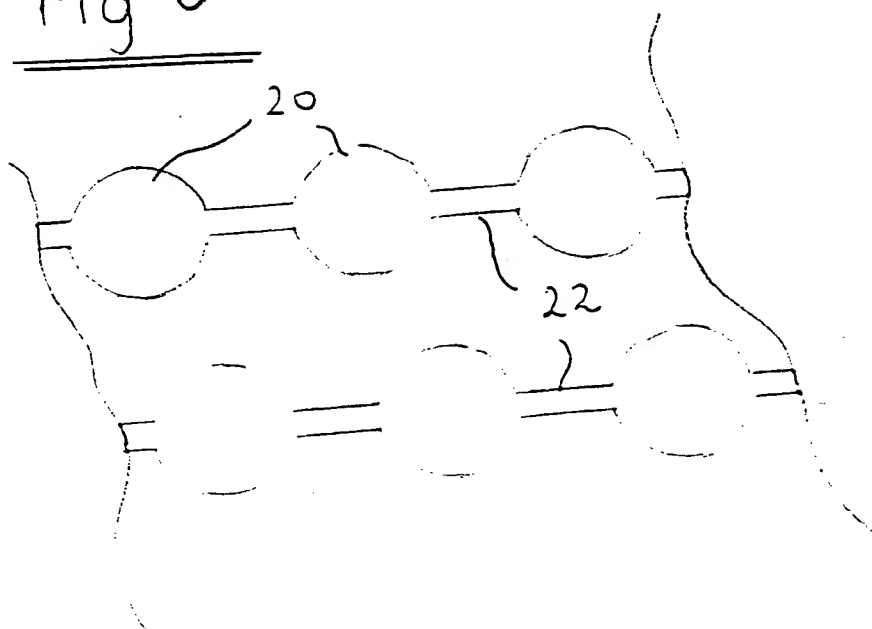


Fig 6



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ATTORNEY DOCKET NO.: FA/153A

SUBSTITUTE

UNITED STATES PATENT APPLICATION

OF

DAVID GEORGE HALLEY, GEORGE MACLEAN CLARKSON
AND JOHN EDWARD TROUBA

FOR

WATER VAPOUR PERMEABLE COMPOSITE MATERIAL

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference P07816PC	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/GB 97/ 02172	International filing date (day/month/year) 12/08/1997	(Earliest) Priority Date (day/month/year) 15/08/1996
Applicant W.L. GORE & ASSOCIATES (UK) LTD. et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. ☐ Certain claims were found unsearchable (see Box I).

2. ☐ Unity of invention is lacking (see Box II).

3. ☐ The international application contains disclosure of a **nucleotide and/or amino acid sequence listing** and the international search was carried out on the basis of the sequence listing

☐ filed with the international application.

☐ furnished by the applicant separately from the international application,

☐ but not accompanied by a statement to the effect that it did not include matter going beyond the disclosure in the international application as filed.

☐ Transcribed by this Authority

4. With regard to the **title**, ☒ the text is approved as submitted by the applicant

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this International Search Report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is:

Figure No. 2 ☐ as suggested by the applicant.

☐ None of the figures.

☒ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

IN NATIONAL SEARCH REPORT

International Application No

PCT/GB 97/02172

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 D06N3/04 D06N3/18 B32B27/12 A41D31/02

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 D06N B32B A41D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 636 423 A (J. S. REID) 13 January 1987 see column 1, line 50 - column 4, line 40 ---	1,30,31, 52
A	EP 0 422 918 A (E.I DU PONT DE NEMOURS AND COMPANY) 17 April 1991 see page 2, line 30 - page 4, line 29 ---	1,15,18, 19,24,28
A	WO 90 15713 A (W. L. GORE & ASSOCIATES, INC.) 27 December 1990 see page 3, line 1 - page 7, line 11 -----	1,18,19, 30,31

☐

Further documents are listed in the continuation of box C.

☒

Patent family members are listed in annex.

° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

24 November 1997

Date of mailing of the international search report

04/12/1997

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Doolan, G

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 97/02172

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4636423 A	13-01-87	NONE	
EP 422918 A	17-04-91	US 5050241 A AT 124326 T AU 620266 B AU 6452090 A CA 2027290 A DE 69020487 D DE 69020487 T JP 3206105 A	24-09-91 15-07-95 13-02-92 18-04-91 12-04-91 03-08-95 07-03-96 09-09-91
WO 9015713 A	27-12-90	CA 2050342 A,C DE 69008723 D DE 69008723 T EP 0476061 A JP 5500641 T US 5104727 A	17-12-90 09-06-94 15-12-94 25-03-92 12-02-93 14-04-92

